Supporting Information

Probing Surface Chemistry at an Atomic Level; Decomposition of 1-Propanethiol on GaP(001)(2×4) Investigated by STM, XPS, and DFT

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Section 1.

Temperature offsets between two measurement methods; thermocouples *vs.* optical pyrometer

In both UHV-STM and XPS systems, sample plates (or chucks) are replaceable from the heater assemblies in vacuum. For instance, in the UHV-STM chamber, a GaP sample (thickness around 250 μm) is placed on top of 1 mm thick Ta sample plate. Underneath, there is a pyrolytic boron nitride (PBN) coated metal wire heater. There is ~1 mm vacuum gap between the Ta sample plate and the surface of the PBN heater though the metal frame enclosing the PBN heater makes direct contact with the sample plate. Thermocouples are fixed on the metal frame around the PBN heater. Thus, the actual sample temperature could be lower than the temperature measured by the thermocouples. Similarly, in the UHV-XPS chamber, the GaP sample is placed on top of a Cu sample chuck using Mo screws. The Cu chuck is replaceable from the heater assembly. The heater and thermocouples were located inside the heater assembly. Thus, there could be temperature offsets between the thermocouple temperatures and the actual sample temperature. The table below shows the temperature offsets measured by the thermocouples and an optical pyrometer. Because the temperature of a Si wafer is more popularly measured by optical pyrometers, we simulated the GaP sample temperature using 250 μm ~ 350 μm thick Si wafers. The Si sample temperature was measured by the optical pyrometer at emissivity of 0.7.

UHV-STM system					
Thermocouples near heaters (K)	473	573	673	773	873
Pyrometer focused on Si sample (K)	446	541	637	733	829
UHV-XPS system					
Thermocouples near heaters (K)	473	573	673	773	873
Pyrometer focused on Si sample (K)	453	554	683	718	798

Section 2.

Substrate-overlayer model

$$\frac{I_{ov}}{I_{sub}} = \left(\frac{SF_{ov}}{SF_{sub}}\right)\left(\frac{\rho_{ov}}{\rho_{sub}}\right)\left[\frac{1-exp\left(-\frac{d_{ov}}{\lambda_{ov}sin\theta}\right)}{exp\left(-\frac{d_{ov}}{\lambda_{sub}sin\theta}\right)}\right] \quad (1)$$

In Equation (1), I_{ov} and I_{sub} indicate the integrated peak areas for the element of interest in the overlayer and substrate, respectively. SF_{ov} and SF_{sub} are the instrument sensitivity factors (0.2780 for C 1s, 0.4453 for S 2p, and 0.2634 for Ga 3d). ρ_{ov} and ρ_{sub} are the molar densities of the atoms in the overlayer and the substrate, respectively. The molar densities of the C and S atoms in the overlayer were estimated from the density of adventitious hydrocarbon (3.3×10^{-10} mol/cm^3)[S1] and molten liquid sulfur (1.819 g/cm^3), respectively. The molar density of Ga atoms in the substrate was calculated from the crystalline GaP density (4.14 g/cm^3). d_{ov} is the thickness of the overlayer. λ_{ov} and λ_{sub} indicate the escape depths of the photoelectrons originating from the orbitals of the atoms of interest located in the overlayer and substrate, respectively. Finally, θ is the take-off angle between the photoelectron detector and the sample surface (fixed at 45° in the current report).

The escape depths of the photoelectrons through the molecular overlayers were approximated by an attenuation length (λ), which is calculated using the following empirical equation[S2]:

$$\lambda = 0.4a^{1.5}E^{0.5}, \quad (2)$$

where E is the kinetic energy of the photoelectron in eV and a is the diameter of the atoms in the monolayer in nm. The diameter of the atom in Equation (2) was calculated using Equation (3),

$$a = \left(\frac{A}{1000N_{av}\rho}\right)^{\frac{1}{3}}, \quad (3)$$

where A is the atomic weight in g/mol, N_{av} is Avogadro's number in number/mol, and ρ is the density of the atom of interest in g/cm^3. From the densities introduced above, the diameters of C, S, and Ga were calculated to be 0.256 nm, 0.308 nm, and 0.343 nm, respectively. Using these values, the escape depths of the Ga 3d photoelectrons that pass through the 1-propanethiol overlayers were calculated to be 2.688 nm in S and 2.035 nm in C, respectively. The escape depths of the S 2p and C 1s photoelectrons that pass through the 1-propanethiol overlayer were calculated to be 2.551 and 1.841 nm, respectively.

Section 3.

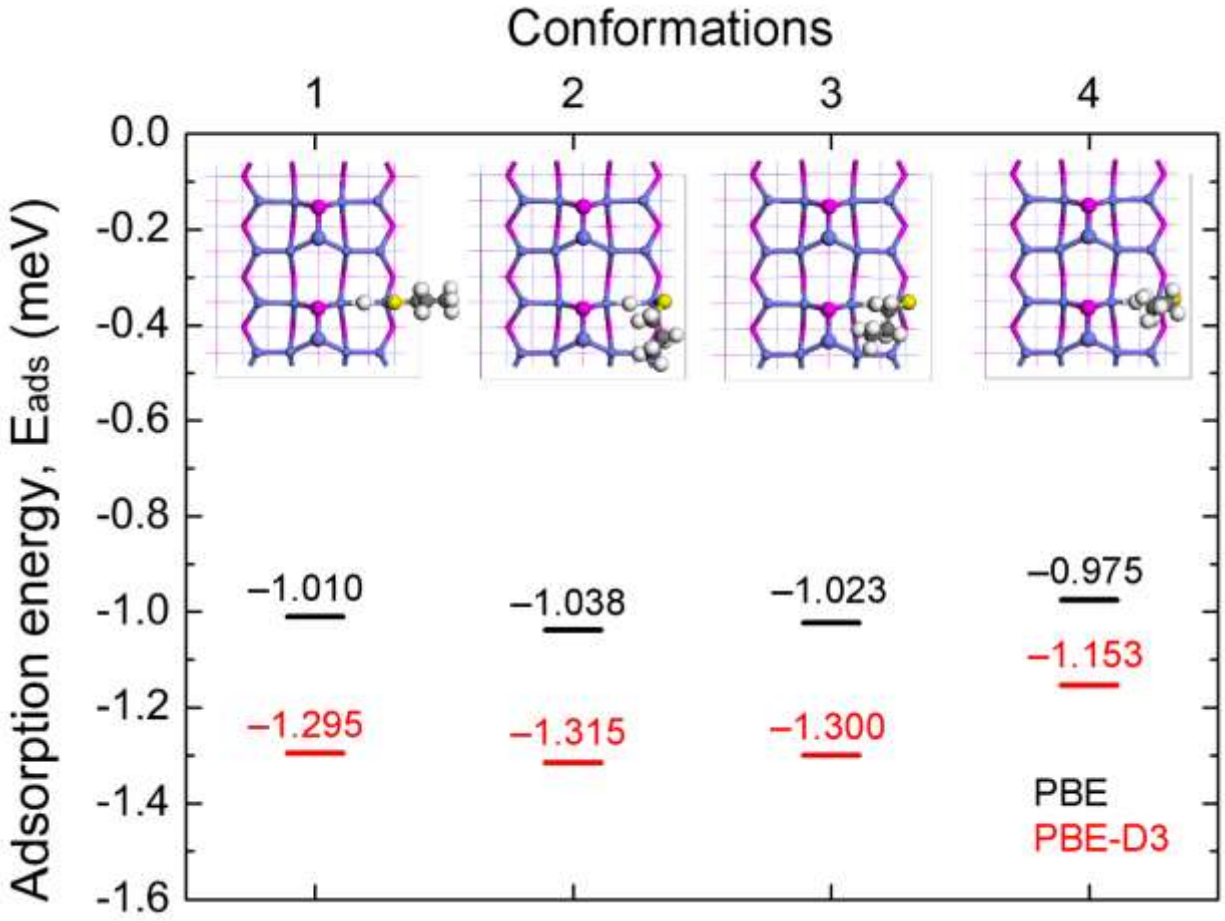

Figure S1. Structures and energies for various conformations of propanethiolate on the 3Ga site and H bridging between the 3Ga and 5Ga sites.

Section 4.

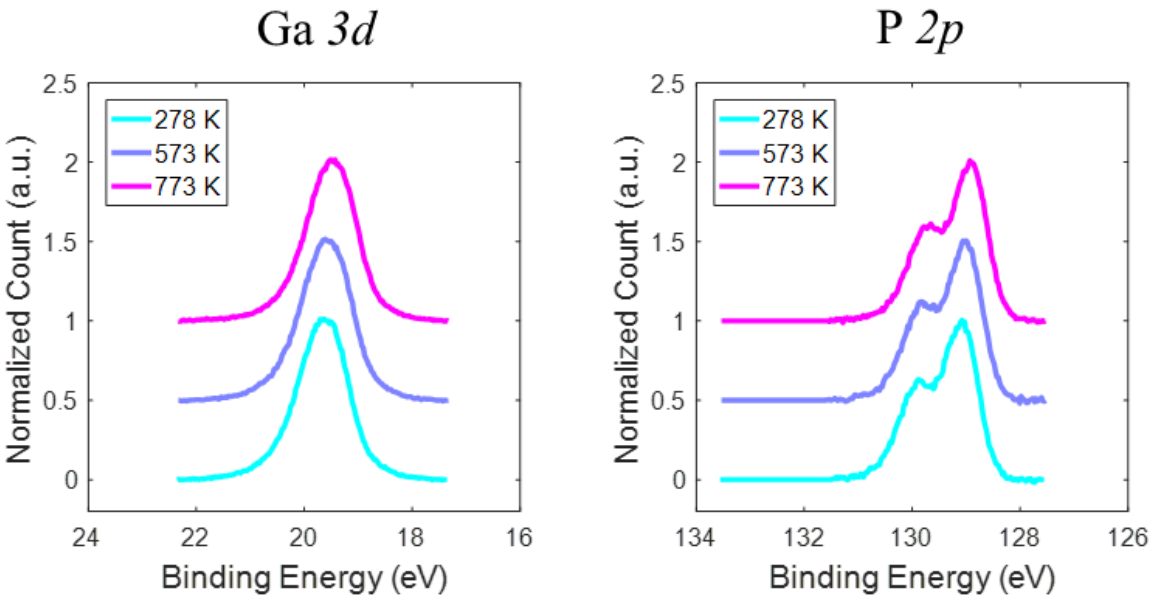

Figure S2. Ga 3*d* and P 2*p* X-ray photoelectron spectra the for 1-propanethiol/GaP(001) samples in Figure 4.

Section 5.

Analysis of adventitious carbon contamination while transferring samples from UHV-STM to UHV-XPS systems.

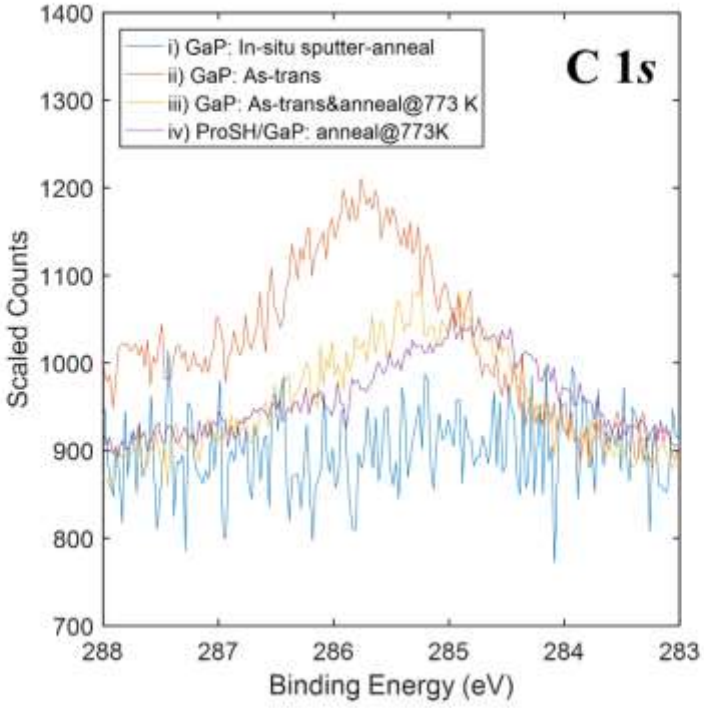

Figure S3. C 1*s* X-ray photoelectron spectra of variously prepared GaP samples. i) A GaP(001) sample was cleaned by several cycles of Ar ion sputtering and annealing at 773 K in UHV-XPS system. ii) A GaP(001) sample was cleaned in the UHV-STM system and transferred to the UHV-XPS system using the sample transfer chamber as described in 2.1 Experimental Details. iii) The sample prepared in ii) was further annealed at 773 K for 30 min in the UHV-XPS system. iv) The 773 K-annealed propanethiol/GaP sample in Figure 4. For i) − iv), the XP spectra were collected at the analyzer angle of 0° against the surface normal direction. For comparison of the spectra obtained at various conditions (i ~ iv), the scaled counts were obtained by dividing the raw data counts with the background photoelectron counts which were calculated by averaging the photoelectron counts at the binding energy from 282.5 to 283.5 eV.

Section 6.

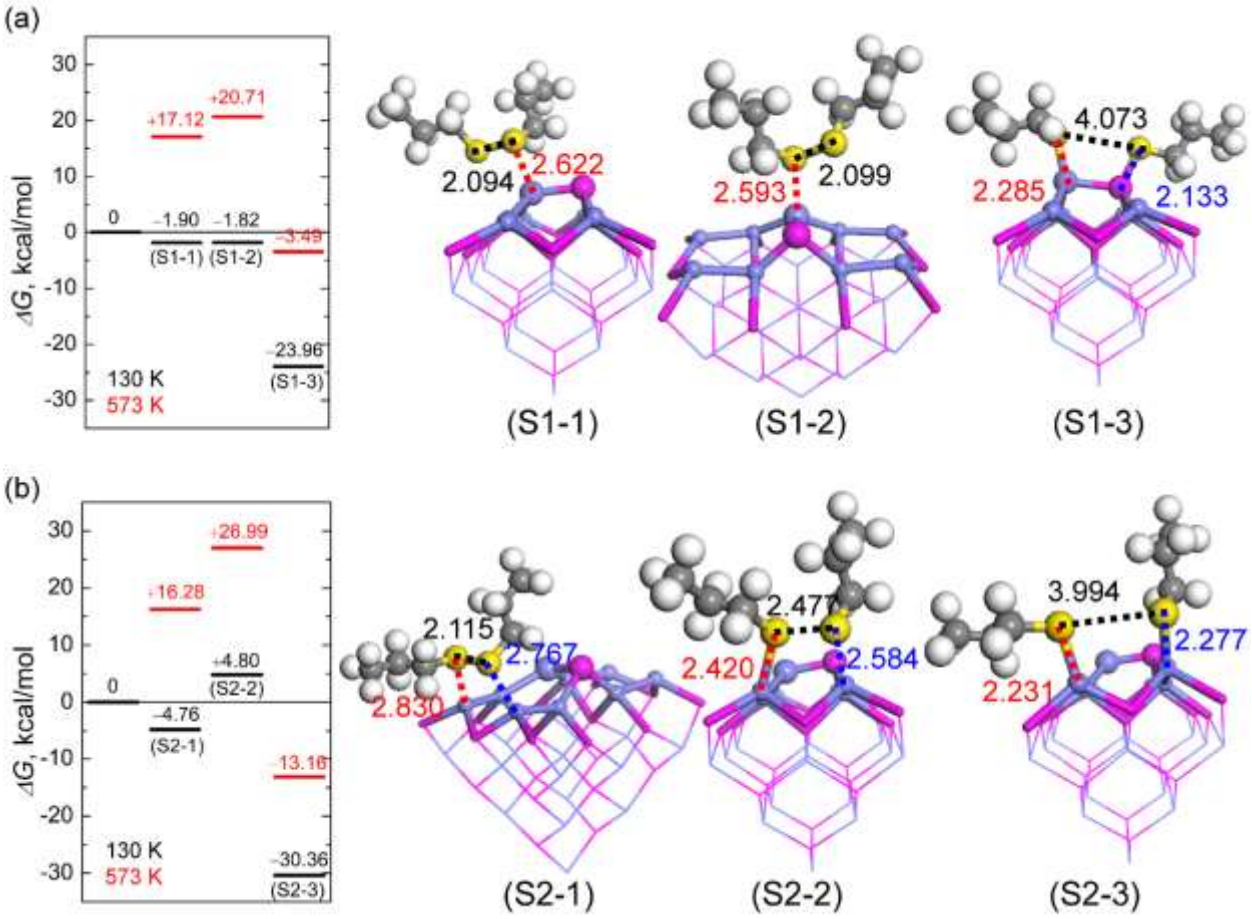

Figure S4. DFT calculations for disulfide bond dissociation of dipropyldisulfide on GaP(001). (left) Gibbs free energy diagram at 130 K in black and 573 K in red and (right) the structures for the 1,2-dipropyldisulfide adsorption and dissociation pathways on the top (a) mixed-dimer site and the edge (b) gallium dimer site of the $Ga_{25}P_{21}H_{30}$ cluster. Numbers in parentheses in the energy diagrams are the structure number. The adsorbed complex before dissociation (left), transition state for the dissociation (middle), and the complex after thiol dissociation (right). White for H, yellow for S, gray for C, magenta for P, and violet for Ga. H atoms at the truncation of the cluster for

charge balance are not shown for simplicity. The atoms in the first two layers are highlighted by a ball-and-stick model. Numbers below the structures denote the distance in Å.

REFERENCES

(S1) Tufts, B.J.; Kumar, A.; Bansal, A.; Lewis, N. S. X-Ray Photoelectron Spectroscopic Studies of Interfacial Chemistry at N-Type Si Liquid Junctions. *J. Phys. Chem.* **1992**. *96*, 4581-4592.

(S2) Briggs, D.; Seah, M. P. *Practical Surface Analysis: Auger and X-ray Photoelectron Spectroscopy*; 2nd ed.; Wiley: New York, 1990.